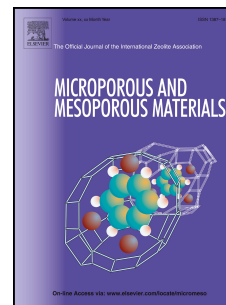


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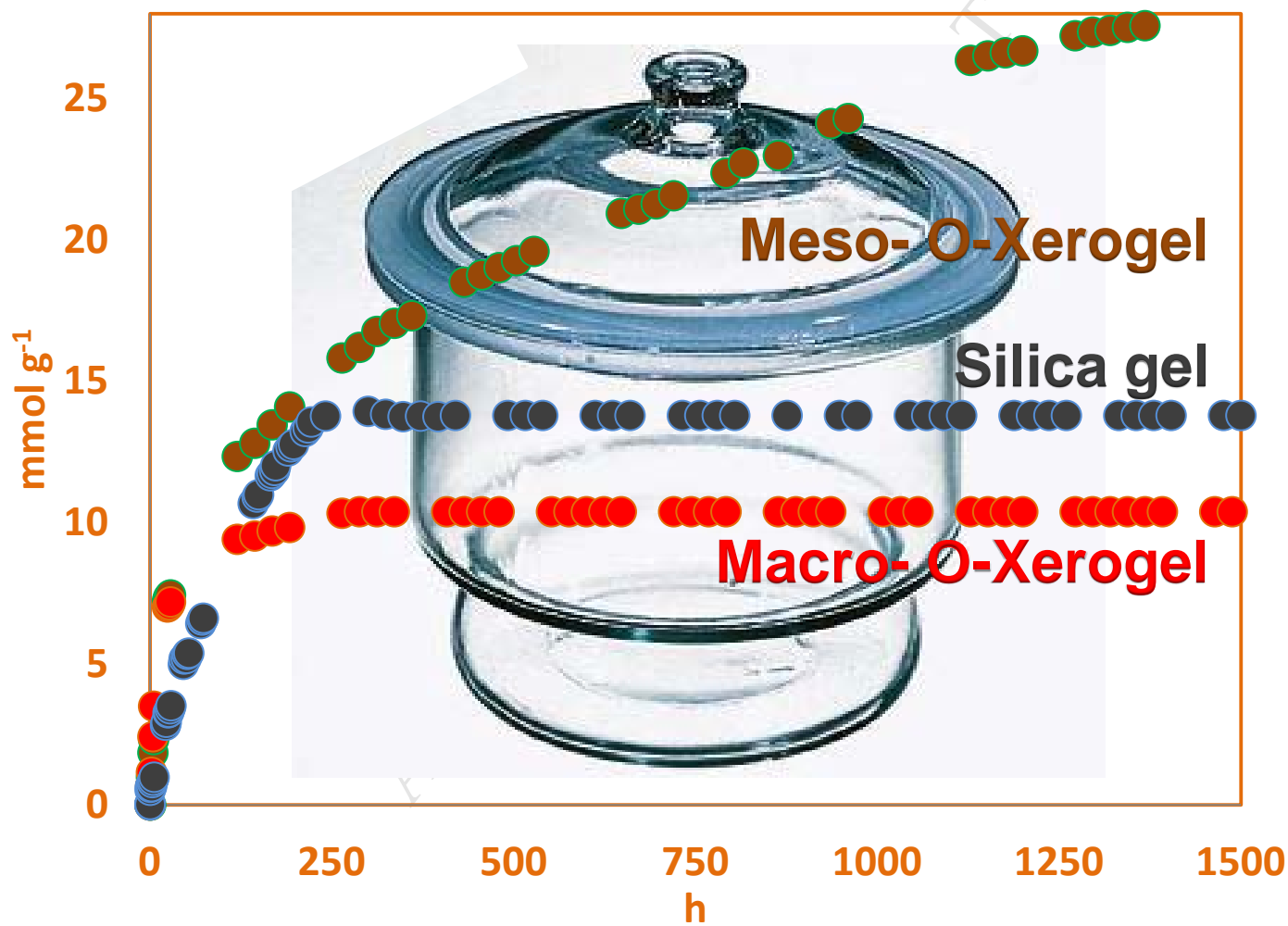
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Desiccant capability of organic xerogels: surface chemistry vs porous texture

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Abstract

Resorcinol-Formaldehyde xerogels are organic polymers that can be easily tailored to have specific properties. These materials are composed of carbon, hydrogen and oxygen, and have a surface that is very rich in oxygen functionalities, and is therefore very hydrophilic. Their most interesting feature is that they may have the same chemical composition but a different porous texture. Consequently, the influence of porous characteristics, such as pore volume, surface area or pore size can be easily assessed. In this work, a commonly used desiccant, silica gel, is compared with organic xerogels to determine their rate and capacity of water adsorption, and to evaluate the role of surface chemistry versus porous texture. It was found that organic xerogels showed a higher rate of moisture adsorption than silica gel. Pore structure also seems to play an important role in water adsorption capacity. The OX-10 sample, whose porosity was mainly composed of micro-mesoporosity displayed a water adsorption capacity two times greater than that of the silica gel, and three times higher than that of the totally macroporous xerogel OX-2100. The presence of feeder pores (mesopores) that facilitate the access to the hydrophilic surface was observed to be the key factor for a good

desiccant behaviour. Neither the total pore volume nor the high surface area (i.e. high microporosity) of the desiccant sample, is as important as the mesopore structure.

Keywords: water sorption; desiccant materials; xerogels; hydrophilic materials

1. Introduction

Organic gels are nanoporous materials that are obtained by the polymerization of hydroxylated benzenes and aldehydes in the presence of a solvent following Pekala's method [1]. Most organic gels presented in literature are synthesized using resorcinol (R) and formaldehyde (F) as precursors and water as solvent [2-5], although other precursors and reaction media can be used [6-9], to produce materials with different properties. In general, three main steps are involved in the formation of the organic gel: gelation, curing and the drying step. Depending on the drying method applied to remove the solvent, gels are classified into three main categories: aerogels, cryogels and xerogels where supercritical drying, freeze-drying and evaporative drying are employed, respectively [5, 10-15]. In this study, microwave radiation was used as heating source throughout the entire synthesis process to produce RF xerogels by means of a simple, fast and cost-effective methodology [16,17].

Over the last few years, organic and carbon xerogels have been demonstrated to be materials of great added value owing to the fact that their porosity can be controlled and designed by adjusting the synthesis variables, both physical (i.e. temperature, time of synthesis, etc.) [2, 16] and chemical (pH, dilution, R/F ratio and percentage of stabilizer contained in the formaldehyde solutions) [17-22]. In addition to the large number of

variables that need to be controlled, it has been shown that there exists a synergy between them. For this reason, statistical programs have been applied to allow the simultaneous study of all of these variables, allowing to designed porous properties for specific applications [18, 21].

Not only is an appropriate porosity necessary for obtaining an optimum material for a specific application, but the surface chemistry also plays an important role. Most of the applications of RF xerogels are based on its carbonized form, for example: electrode material for supercapacitors, hydrogen storage, catalysis, heavy metal adsorbents, etc. [3, 23-28]. As the structure of carbon xerogel is mainly made up of carbon colloidal chains (with a C content of up to 95%), sometimes the material is doped with heteroatoms, or chemically treated to change the surface chemistry and improve its behavior for a specific application [29-32].

The surface chemistry of organic xerogels is different to that of their carbonized counterparts [20]. When polycondensation between resorcinol and formaldehyde takes place, a high concentration of hydroxyl groups remains on their surfaces. Thus, the chemical composition of a generic RF organic xerogel could be 65 % wt. C, 5 % wt. H and 30 % wt. O. However, heat treatment of organic xerogels to obtain a thermally stable material (i.e. carbon xerogel) causes these labile oxygen surface groups to be released, leading to a more condensed carbonaceous structure consisting of about 95 % wt. C, the remaining being divided between H and O [23]. Therefore the surface chemistries of organic and carbon xerogels are totally different, even though their designed porosities may be similar [33, 34].

Desiccant materials are hygroscopic solids that induce or sustain a state of dryness in the surrounding air [35]. In order to be considered a good desiccant porous material, it not only needs to be hydrophilic but also highly adsorbent, which are two different concepts [35]. Its hydrophilicity refers to its affinity to water, while its adsorption capacity depends mainly on its porosity. For example, some carbon-based materials, though considered as hydrophobic, nevertheless have a high water sorption capacity due to their high porosity, but their rate of adsorption is low because their surface chemistry is not appropriate for attracting moisture.

Generally speaking, there are two types of desiccant materials: (i) substances whose desiccant behavior originates from a chemical hydration reaction, such as P_4O_{10} , $MgSO_4$, and (ii) substances whose desiccant behavior is based on surface interactions like adsorption processes. The latter category includes molecular sieves, silica gels, clays and starches [35-37]. The water adsorption behavior of a sorbent depends on many factors, such as the porous structure, chemical composition, surface functionality content, presence of charged species, etc. [32].

Desiccants have been used in recent times for a wide range of applications, with the aim of controlling the humidity in the air when a moisture-free ambient is necessary. Other examples include the use of desiccant materials for controlling the level of water in industrial gas streams, in air conditioner systems, for storing and protecting goods in shipping containers against moisture damage (e.g., electronic devices, foods, clothes, etc.) [38].

As mentioned above, silica gel is the most common desiccant as its chemical behavior has been known since the XVII century and it has been used as a dehumidifier since the beginning of the XX century up to this day. Its good moisture adsorption capacity is due to its porous properties and the presence of hydroxyl groups on its surface which give it a hydrophilic nature. Water molecules are attracted by its surface chemistry which is rich in oxygen.

Due to the physical and chemical similarities between silica gels and RF organic gels, the aim of this work is to evaluate the desiccant behavior of two bare RF xerogels with different porosities. The interest shown in these RF xerogels is due to a series of advantages that they offer, such as their light weight, the possibility of modifying their surface chemistry to enable them to adsorb (and eliminate) components other than moisture, their chemical resistance to acids that may be present in the fluids to be treated, and the fact that they do not require neither doping or post-treatment processes, such as carbonization or activation, which makes them more cost-effective.

2. Experimental Section

2.1. Synthesis of organic xerogels

The organic xerogels used in this study were synthesized by the polymerization of resorcinol (R) and formaldehyde (F), using deionized water as solvent and NaOH as catalyst. First of all, resorcinol (Indspec, 99.6 %) was dissolved in deionized water in an unsealed glass beaker under magnetic stirring until completely dissolved. Then, a formaldehyde solution was added until a homogeneous solution was obtained. The R/F molar ratio used was 0.15 and 0.70 for the synthesis of the samples OX-10 and OX-

2100, respectively. NaOH solution (0.1 M, Titripac, Merck) was added in each precursor solution dropwise until the desired pH was reached. In this case, a pH of 5.8 and 4.8 were selected for the preparation of samples OX-10 and OX-2100, respectively. The precursor solutions were placed in an open vessel inside a microwave oven at 85 °C for about 3 hours in order for gelation and ageing to take place. The polymers were then dried also by microwave heating, in the initial vessel, until a mass loss of over 50 % were recorded, the total time of synthesis being less than 5 h. As a result two different organic gels were obtained with a total yield in the whole process of 45 wt%.

2.2. Sample characterization

Before characterization, the xerogels were outgassed (*Micromeritics VacPrep 0.61*) at 0.1 mbar and 120 °C overnight in order to remove any humidity and other physisorbed gases.

2.2.1. Porous properties

The porosity of the samples was characterized by means of nitrogen adsorption-desorption isotherms and mercury porosimetry.

The nitrogen adsorption-desorption isotherms were measured at -196 °C in a *Tristar 3020* (*Micromeritics*) device. S_{BET} was determined from the N_2 adsorption branch and, in all cases; the number of points used to apply the BET equation was higher than 5.

V_{micro} was estimated by the Dubinin-Raduskevich method [39]. This method only takes into account micropore surfaces. The external surface area (S_{EXT}) was determined by applying the *t*-plot method developed by Lecloux et al. [40], which measures the external surface of the meso-macropores but excludes the microporous surface area.

These two techniques are therefore complementary. N_2 adsorption-desorption isotherms

were only used to obtain information about microporosity (S_{BET} , V_{micro} and mean micropore size) and the S_{EXT} . Parameters, such as porosity (%), pore size distribution (PSD), bulk density and mesopore/macropore volumes (V_{meso} , V_{macro}), were determined by means of mercury porosimetry, using an *AutoPore IV 9500 (Micromeritics)*, which is able to measure from atmospheric pressure up to 228 MPa. In this study, the lowest limit of mesopores detected by this apparatus was 5.5 nm, whereas V_{macro} referred to porosity ranging from 50 to 10000 nm. The surface tension and contact angle were 485 mN m⁻¹ and 130°, respectively, and the stem volume was between 45-58 % in all the analyses performed. In the low pressure step, the samples were evacuated up to 6.7 Pa. The equilibration time used was 10 seconds.

2.2.2. Elemental analysis

Determination of C, H and N was carried out in a *LECO CHNS-932* analyzer. The oxygen content was determined using a *LECO VTF-900* analyzer.

2.2.3. TPD analysis

The typology of the surface oxygen groups contained in the RF xerogels was evaluated by temperature programmed desorption (TPD) using a Chemisorption *Autochem II 2920* device from *Micromeritics*. This equipment is a fully automated chemisorption analyzer, which includes a gas feeding system, a temperature-controlled reaction zone and a gas analyzer (mass spectrometer, OmniStar TM, Pfeiffer Vacuum). The amount of CO and CO₂ released was registered while the samples were subjected to heat treatment from room temperature to 1000 °C at a heating rate of 10 °C min⁻¹ under an Ar flow of 50 mL min⁻¹.

2.2.4. FTIR analysis

Surface chemistry was also characterized by Fourier transform infrared spectroscopy (FTIR) in a Nicolet FTIR 8700 with DTGS detector. The data were recorded between 4000-400 cm^{-1} , using 64 scans and a resolution of 4 cm^{-1} .

2.2.5. Water vapour adsorption experiments

The procedure for measuring the capacity of water vapour adsorption and kinetics consisted in placing 0.6-0.8 g of sample inside a hermetic vessel at 25 °C and 100 % humidity and recording changes in mass with time until constant values were reached. Water vapour adsorption-desorption isotherms were obtained using a Hydrosorb 1000 multigas instrument (Quantachrome) at 25 °C.

3. Results and Discussion

3.1. Porous properties

For comparative purposes a commercial silica gel, commonly used as desiccant in laboratories, was selected (Sigma-Aldrich, 2-6 mm particle size). The data relating to the textural properties of the two RF organic xerogels and the selected desiccant reference (i.e. silica gel) are presented in Table 1. These differences on the porosity between these xerogels are consequence of the variables used for each sample during the synthesis process, as can be found in literature [17, 18, 21]. Differences between the micro-mesoporosities of the samples were determined from N_2 adsorption-desorption isotherms, as shown in Figure 1. The silica gel used for this study is a micro-mesoporous material with an average mesopore size of ca. 4 nm, a value extracted from the PSD obtained by applying the DFT method to the adsorption branch of the nitrogen isotherm (data not shown). The OX-10 xerogel yields an isotherm that can be classified

as type I-IV according to the BDDT classification, although the presence of a hysteresis loop at high relative pressures denotes the presence of a certain macroporosity (a deduction supported by the results of mercury porosimetry). Although the surface area of the silica gel is higher than that of OX-10 (338 versus 214 m² g⁻¹ respectively), the total pore volume and the S_{ext} of OX-10 is higher than that of the silica gel (Table 1), due to the differences in the pore size distributions. According to the N₂ adsorption isotherm corresponding to OX-2100, this sample shows almost no adsorption at all, which does not necessarily mean that it is a non-porous material, but the pore size is too large to be determined accurately by this technique. In this case, porosity was characterised by mercury porosimetry

Figure 2 illustrates the cumulative volume vs. pore size obtained from the mercury porosimetry experiments. As the *Autopore IV* porosimeter cannot detect pores smaller than 5.5 nm, silica gel was not analysed by this technique since it has a narrower pore structure. In Figure 2a, it can be observed that the cumulative volume falls to a pore size of 10-20 nm, which implies that most of the pores in OX-10 are in the mesopore range. However, a small volume of pores larger than this are observed as well corresponding to the macropore range up to 120 nm. From Figure 2b, on the other hand it is clear that the OX-2100 xerogel has a larger pore size, due to a change in cumulative volume corresponding to a pore size of ca. 2100 nm, which denotes a macroporous material. (Figure S1 in Supplementary Material shows the pore size distributions for both RF xerogels: OX-10 and OX-2100).

In short, the three samples used in the present study possess totally different porous structures, as the silica gel is a micro-mesoporous material with narrow mesopores, OX-10 is micro-meso-macroporous while OX-2100 is entirely macroporous.

3.2. Chemical properties

The data obtained from the elemental analysis of the organic xerogels are presented in Table 2. As can be seen, the chemical composition is very similar in both samples. From the elemental analysis data it can be inferred that the O/C molar ratio for the organic xerogels is 0.35. Their high oxygen content makes it necessary to examine the typology of these groups in order to determine whether the different synthesis conditions affect the nature of the oxygenated groups.

The quantity and type of oxygen functionalities in the organic xerogels can be determined from the TPD curves, since the oxygen groups decompose into CO and CO₂ upon heating. According to Figure 3, the evolving CO and CO₂ groups are virtually identical in both cases, which implies that not only is the proportion of oxygen very similar in both samples but that the type of oxygen functionality is practically identical as well. Therefore, to obtain RF xerogels with different surface chemistries, some post-treatments must be performed.

In general, it can be observed that both organic xerogels have a larger quantity of oxygen groups desorbing as CO, namely, neutral or basic groups (phenols, alcohols) [41, 42], which is in agreement to the most abundant oxygen surface groups in RF

xerogels. In the CO evolution curves of Figure 3, both samples show a very pronounced peak centred at ca. 650 °C, which can be assigned to phenols (-OH), since according to the literature groups of this type evolve as CO in a temperature range of 500-750 °C [42].

The less stable and more acidic functionalities (carboxylic acids, anhydrides, lactones) produce CO₂ when the material is subjected to thermal treatment. The CO₂ spectrum indicates a clear less presence of the oxygen functionalities that release as CO₂. Two peaks can be recognized, one whose maximum is around 350 °C, can be attributed to a small presence of carboxylic acids whereas the other centred at around 550 °C, suggests the presence of carboxylic anhydride and/or lactone-type groups [41, 42]. These functionalities may be produced, in a small extent, during the drying step in air by microwave heating.

FTIR may also provide some information about the functionalities present in the samples studied. Figure 4 shows analogous spectra for the two organic xerogels, confirming the similar composition and functionalities of both samples. In both cases, there is a broad band between 3600 and 3000 cm⁻¹ associated to the O-H stretching vibrations, originating from the phenol groups. Aliphatic stretching vibrations can be assigned to the band at 2900 cm⁻¹, whilst the corresponding aliphatic deformation vibration is located at ca. 1400 cm⁻¹. The well defined band at around 1600 cm⁻¹ corresponds to the aromatic ring stretching vibration C=C. Bands at 1100 and 1200 cm⁻¹ are assigned to methylene ether bridges C-O-C stretch and =C-O-C symmetric and

asymmetric stretch. C-O stretching from alcohols also contribute with bands at 1100 cm^{-1} , whilst and small contribution from C=O carbonyl stretching from carboxylic acids, anhydrides, ester and ketones are assigned to band ca. 1700 cm^{-1} . All these oxygen functionalities are in agreement with the TPD results mentioned above.

On the other hand, silica gel obviously presents a different spectrum. It can be observed a broad band at around 3400 cm^{-1} due to the hydroxyl group on the surface of the silica. The well defined bands at 470 and 790 cm^{-1} are ascribed to the Si-O-Si bending vibrations, whilst the broad band at ca. 1100 cm^{-1} is due to the Si-O stretching.

3.3. Desiccant behaviour

The desiccant properties of silica gel are due to the presence of hydroxyl groups in the surface of the material that endow it with a hydrophilic nature. Moreover, its porosity gives it a high water adsorption capacity so that moisture is attracted and retained in the surface of the material. The results of this study show that organic xerogels are materials with a potential desiccant capacity since they contain mainly phenolic groups on their surface (see Figures 3 and 4), and have a porous structure that can be tailored to optimize the adsorption of water.

The desiccant behaviour of the samples at $25\text{ }^{\circ}\text{C}$ under atmospheric pressure and 100% humidity is illustrated in Figure 5. As can be observed, the slope of the organic xerogels curves during the first few hours is steeper, which implies that the speed of adsorption is

faster in both samples. Taking into account that all the oxygen content may contribute to the hydrophilic character in a sample, it can be made a rough estimation of the oxygen content ratio in the samples studied. Thus, from the theoretical formula of silica gel (i.e., $\text{SiO}_2 \cdot n\text{H}_2\text{O}$) it can be estimated that the O/Si molar ratio may be considered as 2. In spite of the fact that the proportion of oxygen is lower in the case of xerogels ($\text{O/C} = 0.35$ for organic xerogels and $\text{O/Si} = 2$ for silica gel), water is more easily attracted to the surface of organic xerogels than in the case of silica, due to either their surface chemistry or their different porous structure which is characterised by the presence of feeder pores, or to a combination of both of these factors.

Once the first hours (ca. 48 h) have elapsed, greater differences between the samples become apparent. The RF xerogel labelled OX-2100, which is a totally macroporous sample, allows water molecules easy access to its surface but, once all of the surface is covered, the speed of adsorption decreases drastically and saturation point is reached at ca. 10 mmol/g. Silica gel starts with a lower rate of adsorption, and its capacity of adsorption is sharply reduced at around 14 mmol/g after 250 h. This could be because the water molecules experience greater difficulty accessing the narrow pores. Nevertheless its large surface area provides a readily available surface area covered with hydroxyl groups with an affinity for water molecules.

Not only does sample OX-10 show a faster rate of water adsorption but it also has a better water adsorption capacity than the other two samples. Although the rate of adsorption decreases progressively, the sample keeps adsorbing moisture for more than 1200 h. The OX-10 sample adsorbs ca. 27 mmol/g which amounts to 50 % of its own weight in water.

The desiccant materials employed in this study are substances whose performance as desiccants is based on surface interactions like those of adsorption processes. It is for this reason that these materials can be regenerated merely by heating, enabling them to be reused several times. Accordingly, the temperature of regeneration is a factor that must be taken into account especially when their application is intended for industrial scale. The advantage of silica gel and RF organic xerogels is that they can be regenerated by heating at relatively low temperatures (i.e. 120°C), whilst other desiccants commonly used, such as alumina require higher regeneration temperatures.

It is well known that at ambient pressure water molecules do not condense in pores and fill the entire pore volume. This would suggest that the total pore volume is not the main factor that determines the desiccant behaviour of these materials. Nevertheless, despite the importance of hydroxyl surface groups in determining the hydrophilic character of the material, the pore structure is also relevant as this affects the rate of adsorption and the availability of the hydrophilic surface in desiccants.

Further insights into the hydrophilic behaviour of the materials were obtained from the water adsorption isotherms at 25 °C (Figure 6). As expected, the maximum water uptakes measured during the dynamic (Figure 5) and equilibrium (Figure 6) experiments agree reasonably well (i.e. 27 vs 20 mmol g⁻¹, 14 vs 11 mmol g⁻¹, 10 vs 8 mmol g⁻¹ for OX-10, Silica gel and OX-2100 in the dynamic vs equilibrium experiments). At low relative pressures ($p/p^0 < 0.25$, Figure 6), the amount of water adsorbed on both the organic xerogels and the silica gel is essentially the same. This result indicates that differences in microporosity (see Table 1) are not determinant for

the adsorption of water molecules. Adsorption by the silica gel increases smoothly from $p/p^0 > 0.25$, whereas the water adsorption isotherms of the two OXs remain identical up to $p/p^0 = 0.9$, probably due to the presence of wider pores in the organic xerogels. The silica gel has a narrow mesoporosity (mean pore size 4 nm according to DFT calculations), that comes into play at lower relative pressures. The presence of wider mesopores (i.e. mean pore size 10 nm according to mercury porosimetry) in the OX-10 sample causes its water capacity to increase dramatically in the $0.9 < p/p^0 < 1$ interval, whilst sample OX-2100 displays the lowest total water adsorption capacity of the series studied due to the fact that its pores are too wide to play an important role in the adsorption of water. The water vapor adsorption isotherm obtained for this sample (OX-2100) is corroborated by others in the literature [43] corresponding to RF-xerogels with similar porosity that is not adequate for water adsorption applications. Therefore, although all RF-xerogels present hydrophilic character, not all of them can be used as desiccants but only the ones with the proper porosity.

4. Conclusions

The desiccant behaviour of two organic xerogels with different porosities was studied and compared using silica gel as reference material. Although the presence of hydroxyl groups in the organic xerogels may be lower than in the silica gel, the former showed a higher rate of moisture adsorption. Pore structure seemed to play an important role in water adsorption capacity. The OX-10 sample, whose porosity was mainly composed of micro-mesoporosity displayed a water adsorption capacity two times higher than the silica gel, and three times higher than OX-2100, a totally macroporous xerogel. Although the presence of oxygen surface groups is important as it determines the

hydrophilic character of the material, the presence of feeder pores (mesopores) that facilitates access to the hydrophilic surface was found to be the key factor for ensuring a good desiccant behaviour. Neither the total pore volume nor the high surface area (i.e. high microporosity) of the desiccant sample has a greater influence than the mesopore structure.

Moreover, organic xerogels offer a series of important advantages: their light weight, the possibility of modifying the surface chemistry to adsorb (and eliminate) components other than moisture, chemical resistance to acids that may be present in the fluids to be treated, and the possibility of being applied without the need for a doping or carbonization/activation step, making them cost-effective materials.

In short, all organic xerogels are hydrophilic materials since its surface is absolutely covered by oxygenated groups, independently of the variables used during synthesis. The water absorption capacity, which endows these materials of a desiccant behaviour, depends on the porosity of the material which can be controlled with the variables used during the synthesis process. Therefore, not all of them can be used as desiccants since only a proper porosity provides them of this capacity. If porosity is properly designed, organic xerogels are efficient desiccant materials which offer a fast rate of adsorption, a good water adsorption capacity, and can be easily regenerated at low temperature.

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Table 1. Textural properties of the two RF xerogels and the reference silica gel

		OX-10	OX-2100	Silica gel
N₂ Isotherm	$S_{\text{BET}} (\pm 5, \text{m}^2 \text{g}^{-1})$	214	9	338
	$V_{\text{DUB-N}_2} (\pm 0.05, \text{cm}^3 \text{g}^{-1})$	0.08	0.00	0.12
	$V_{\text{p}} (\pm 0.05, \text{cm}^3 \text{g}^{-1})$	1.38	0.02	0.23
	$S_{\text{ext}} (\pm 5, \text{m}^2 \text{g}^{-1})$	187	12	170
Hg porosimetry	$\rho^{\text{a}} (\pm 0.05, \text{g cm}^{-3})$	0.47	0.34	-
	$V_{\text{meso}} (\pm 0.05, \text{cm}^3 \text{g}^{-1})$	0.78	0.00	-
	$V_{\text{macro}} (\pm 0.05, \text{cm}^3 \text{g}^{-1})$	0.56	2.15	-
	$d_{\text{pore}} (\pm 2, \text{nm})$	10	2100	-

Bulk density

a.

Table 2. Elemental analysis results for the two organic xerogels (dry basis)

	OX-10	OX-2100
C (± 0.2 , wt. %)	64.7	66.3
H (± 0.2 , wt. %)	4.9	4.5
N (± 0.2 , wt. %)	0.3	0.3
O (± 0.2 , wt. %)	30.1	28.9

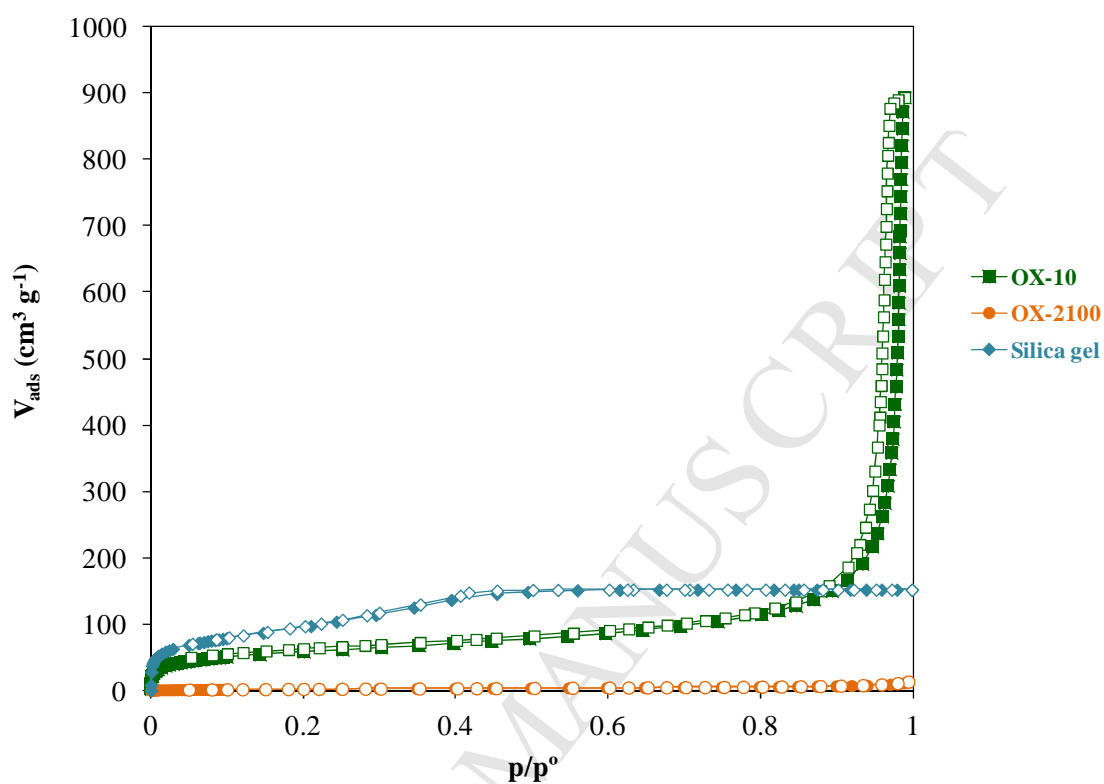


Figure 1. N₂ adsorption–desorption isotherms of the organic xerogels and the reference silica gel sample.

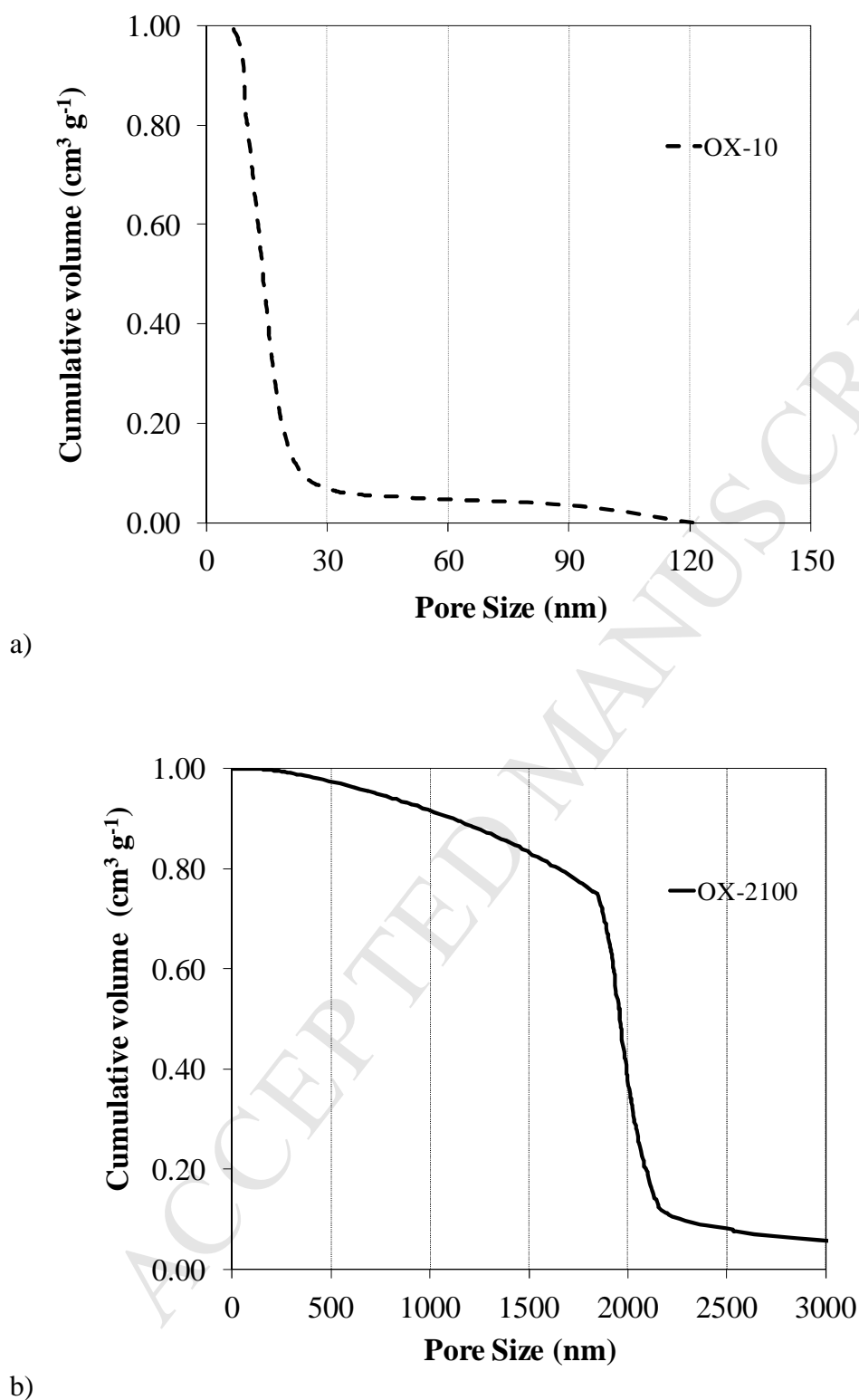


Figure 2. Cumulative volume vs. pore size obtained by mercury porosimetry for the RF xerogels: a) OX-10 and b) OX-2100.

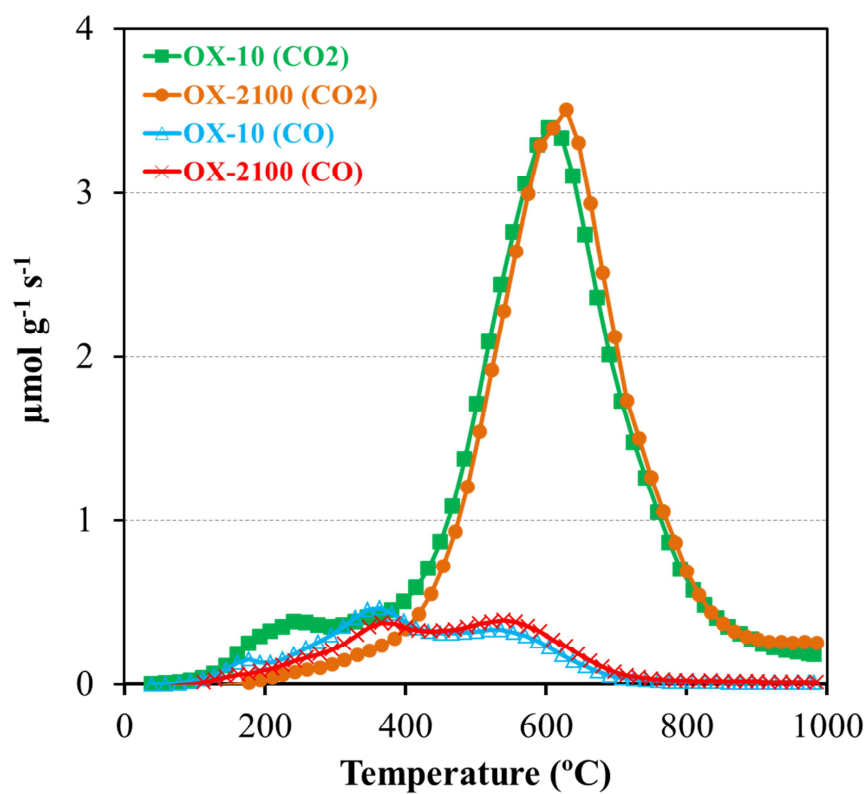


Figure 3. CO and CO₂ TPD spectra of the two organic xerogels OX-10 and OX-2100.

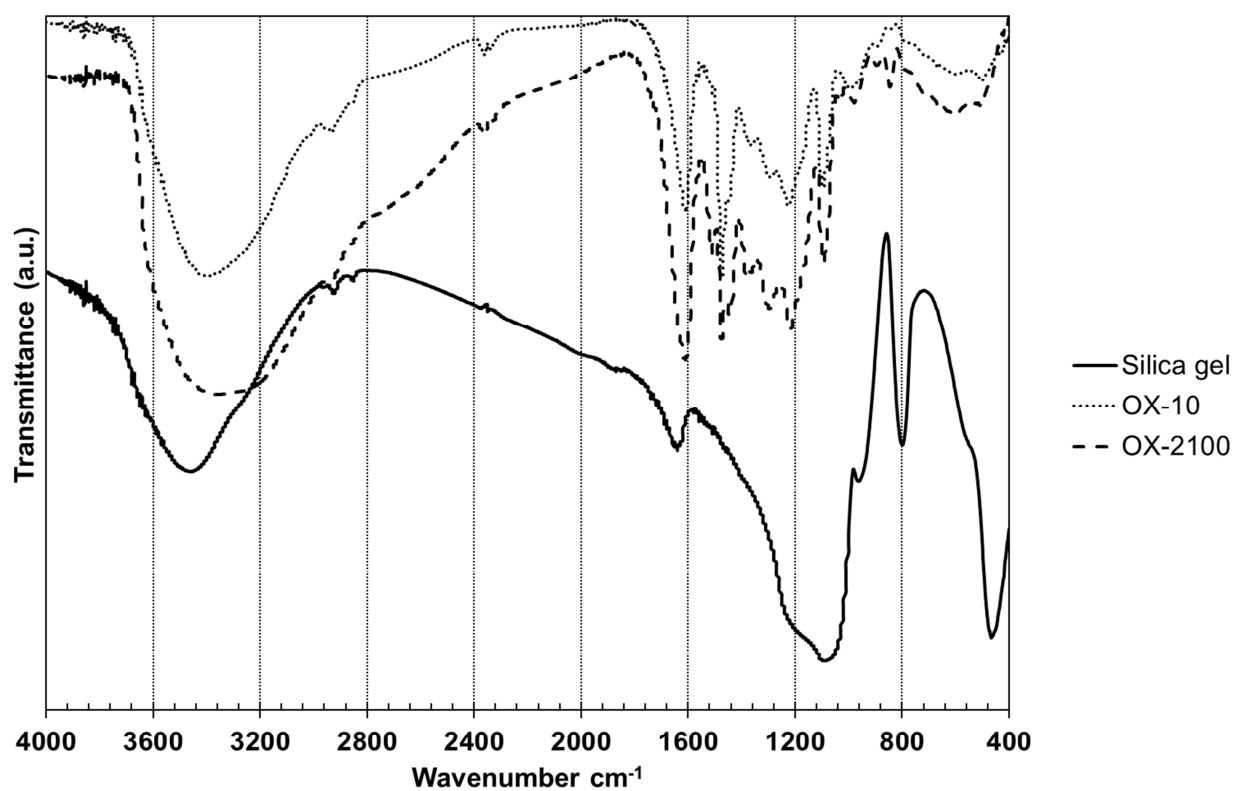


Figure 4. FTIR spectra of the two organic xerogels and the silica gel.

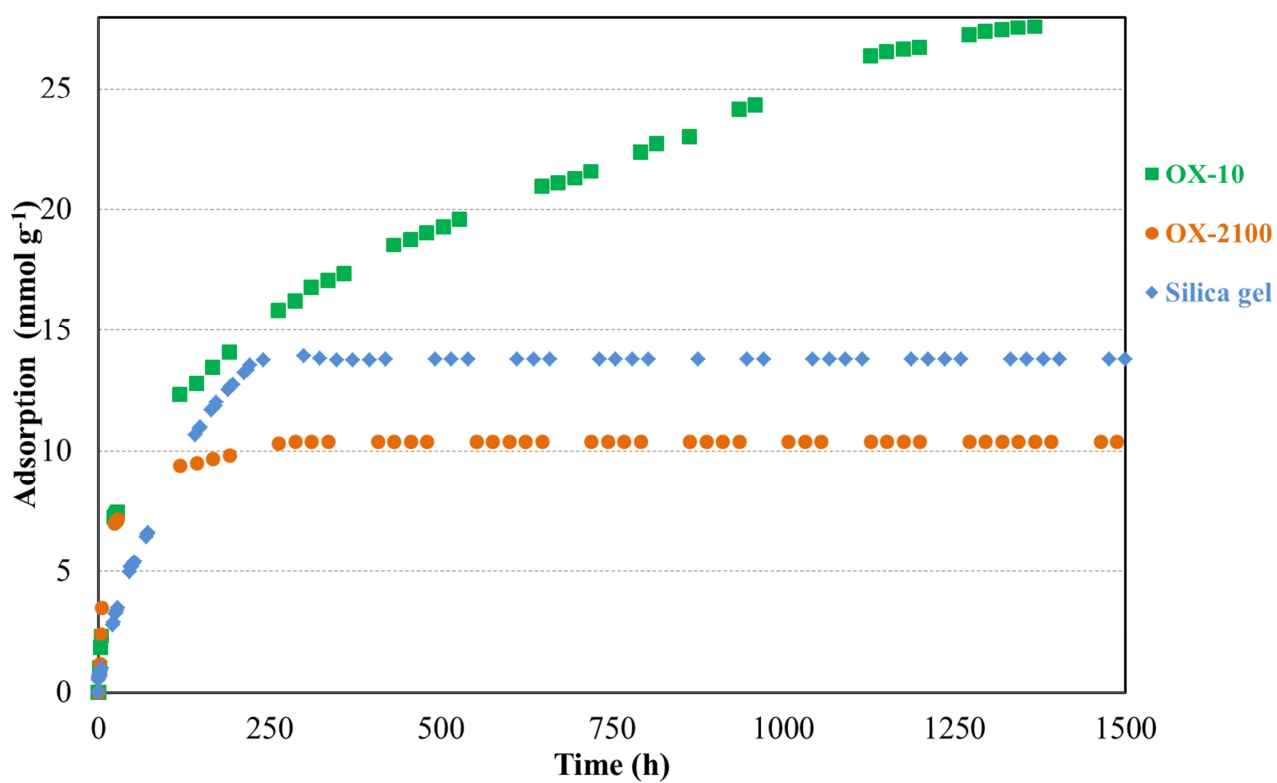


Figure 5. Moisture adsorption isotherms at 25 °C, atmospheric pressure and 100 % humidity corresponding to OX-10, OX-2100 and the silica gel.

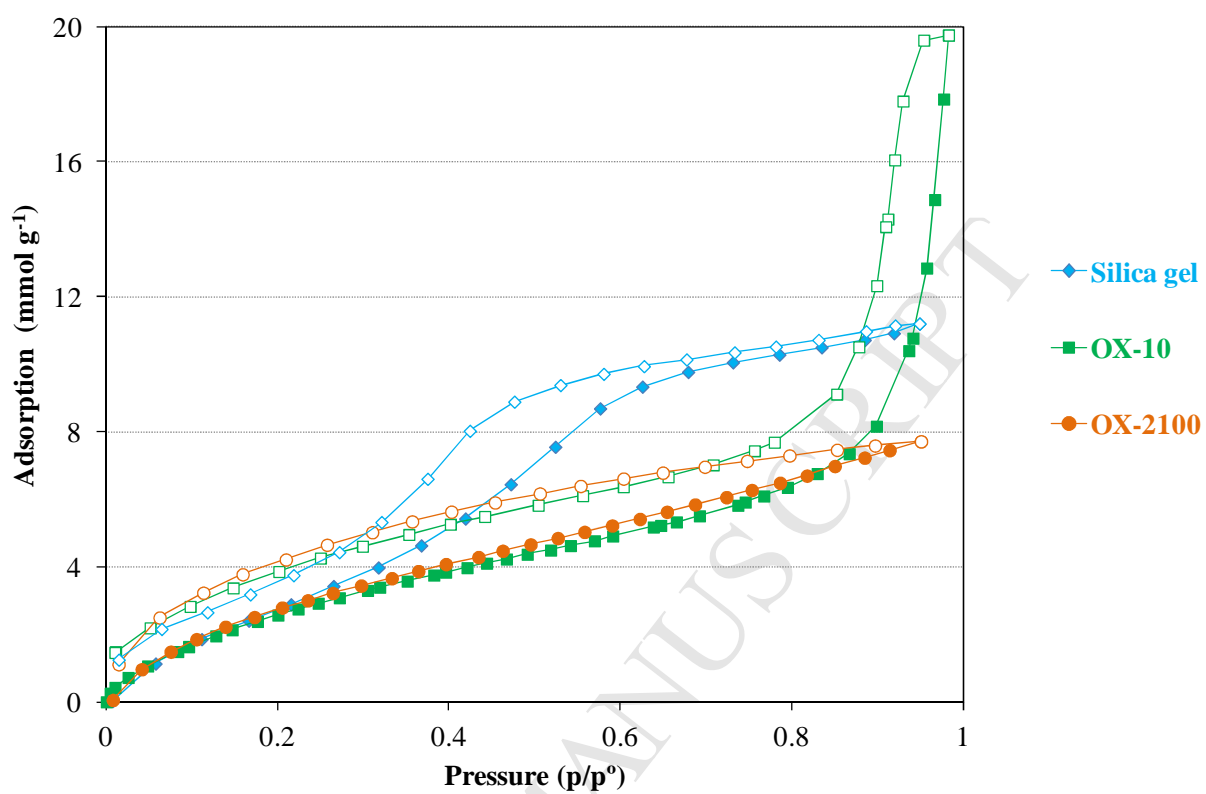


Figure 6. Water adsorption isotherms at 25 °C of the two organic xerogels and the reference silica gel.

HIGHLIGHTS

- RF xerogels showed a higher rate of moisture adsorption than silica gel
- Surface chemistry is important for a good desiccant due to the hydrophilic character
- Mesopore structure is the key factor for a high water adsorption capacity